Claims

1. A proton-conducting polymer membrane comprising polymers containing phosphonic acid groups which is obtainable by a process comprising the steps

A) mixing of vinyl-containing phosphonic acid with one or more aromatic tetraamino compounds with one or more aromatic carboxylic acids, esters thereof, acid halides thereof or anhydrides thereof which contain at least two acid groups per carboxylic acid monomer, and/or
mixing of vinyl-containing phosphonic acid with one or more aromatic and/or heteroaromatic diamino carboxylic acids, esters thereof, acid halides thereof or anhydrides thereof,

B) heating of the mixture obtainable according to step A) under inert gas at temperatures of up to 350°C to form polyazole polymers,

C) application of a layer using the mixture from step A) and/or B) to a support,

D) polymerization of the vinyl-containing phosphonic acid present in the sheet-like structure obtainable according to step C).

2. The membrane as claimed in claim 1, characterized in that 3,3',4,4'-tetraaminobiphenyl, 2,3,5,6-tetraaminopyridine, 1,2,4,5-tetraaminobenzene, bis(3,4-diaminophenyl) sulfone, bis(3,4-diaminophenyl) ether, 3,3',4,4'-tetraaminobenzophenone, 3,3',4,4'-tetraaminodiphenylmethane and 3,3',4,4'-tetraaminodiphenyldimethylmethane are used as aromatic tetraamino compounds.

3. The membrane as claimed in claim 1 or 2, characterized in that isophthalic acid, terephthalic acid, phthalic acid, 5-hydroxyisophthalic acid, 4-hydroxyisophthalic acid, 2-hydroxyterephthalic acid, 5-aminoisophthalic acid, 5-N,N-dimethylaminoisophthalic acid, 5-N,N-diethylaminoisophthalic acid, 2,5-dihydroxyterephthalic acid, 2,5-dihydroxyisophthalic acid, 2,3-dihydroxyisophthalic acid, 2,3-dihydroxyphthalic acid, 2,4-dihydroxyphthalic acid, 3,4-dihydroxyphthalic acid, 3-fluorophthalic acid, 5-fluoroisophthalic acid, 2-fluoroterephthalic acid, tetrafluorophthalic acid, tetrafluoroisophthalic acid, tetrafluoroterephthalic acid,1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, diphenic acid, 1,8-dihydroxynaphthalene-3,6-dicarboxylic acid, bis(4-carboxyphenyl) ether, benzophenone-4,4'-dicarboxylic acid, bis(4-carboxyphenyl) sulfone, biphenyl-4,4'-dicarboxylic acid, 4-trifluoromethylphthalic acid, 2,2-bis(4-carboxyphenyl)hexafluoropropane, 4,4'-stilbenedicarboxylic acid, 4-carboxycinnamic acid, or C1-C20-alkyl esters or

C5-C12-aryl esters thereof, or anhydrides thereof or acid chlorides thereof are used as aromatic carboxylic acids.

4. The membrane as claimed in one or more of the preceding claims, characterized in that tricarboxylic acids, C1-C20-alkyl esters thereof, C5-C12-aryl esters thereof, anhydrides thereof or acid chlorides thereof or tetracarboxylic acids, C1-C20-alkyl esters thereof, C5-C12-aryl esters thereof, anhydrides thereof or acid chlorides thereof are used as aromatic carboxylic acids.

5. The membrane as claimed in claim 4, characterized in that 1,3,5-benzenetricarboxylic acid (trimesic acid); 2,4,5-benzenetricarboxylic acid (trimellitic acid); (2-carboxyphenyl)iminodiacetic acid, 3,5,3'-biphenyltricarboxylic acid; 3,5,4'-biphenyltricarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzene-1,2,4,5-tetracarboxylic acid; naphthalene-1,4,5,8-tetracarboxylic acid, 3,5,3',5'-biphenyltetracarboxylic acid, benzophenonetetracarboxylic acid, 3,3',4,4'-biphenyltetracarboxylic acid, 2,2',3,3'-biphenyltetracarboxylic acid, 1,2,5,6-naphthalenetetracarboxylic acid and/or 1,4,5,8-naphthalenetetracarboxylic acid are used as aromatic carboxylic acids.

6. The membrane as claimed in claim 4, characterized in that the content of tricarboxylic acids and/or tetracarboxylic acids is in the range from 0 to 30 mol%, preferably from 0.1 to 20 mol%, in particular from 0.5 to 10 mol%, based on dicarboxylic acid used.

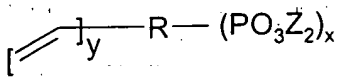
7. The membrane as claimed in claim 1, characterized in that heteroaromatic dicarboxylic acids, heteroaromatic tricarboxylic acids and/or heteroaromatic tetracarboxylic acids containing at least one nitrogen, oxygen, sulfur or phosphorus atom in the aromatic are used as heteroaromatic carboxylic acids.

8. The membrane as claimed in claim 7, characterized in that pyridine-2,5-dicarboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridinedicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2,6-pyrimidinedicarboxylic acid, 2,5-pyrazinedicarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzimidazole-5,6-dicarboxylic acid, and also C1-C20-alkyl esters or C5-C12-aryl esters thereof, or anhydrides thereof or acid chlorides thereof or C1-C20-alkyl esters or C5-

C12-aryl esters thereof or anhydrides thereof or acid chlorides thereof are used.

9. The membrane as claimed in claim 1, characterized in that diaminobenzoic acid and/or monohydrochloride and dihydrochloride derivatives thereof are used as aromatic diamino carboxylic acids.

10. The membrane as claimed in claim 1, characterized in that the mixture prepared in step A) and/or step B) comprises compounds of the formula



where

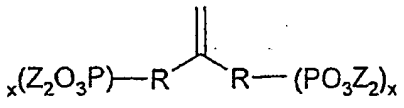
R is a bond, a C1-C15-alkyl group, C1-C15-alkoxy group, ethylenoxy group or C5-C20-aryl or heteroaryl group, with the above radicals themselves being able to be substituted by halogen, -OH, COOZ, -CN, NZ_2,

the radicals Z are each, independently of one another, hydrogen, a C1-C15-alkyl group, C1-C15-alkoxy group, ethylenoxy group or C5-C20-aryl or heteroaryl group, with the above radicals themselves being able to be substituted by halogen, -OH, -CN, and

x is 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10,

y is 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10,

and/or of the formula



where

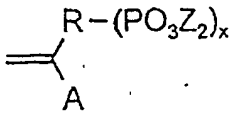
R is a bond, a C1-C15-alkyl group, C1-C15-alkoxy group, ethylenoxy group or C5-C20-aryl or heteroaryl group, with the above radicals themselves being able to be substituted by halogen, -OH, COOZ, -CN, NZ_2,

the radicals Z are each, independently of one another, hydrogen, a C1-C15-alkyl group, C1-C15-alkoxy group, ethylenoxy group or C5-C20-aryl or hetero-

aryl group, with the above radicals themselves being able to be substituted by halogen, -OH, -CN, and

x is 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10,

and/or of the formula



where

A is a group of the formulae $COOR^2$, CN, $CONR^2_2$, OR^2 and/or R^2, where R^2 is hydrogen, a C1-C15-alkyl group, C1-C15-alkoxy group, ethylenoxy group or C5-C20-aryl or heteroaryl group, with the above radicals themselves being able to be substituted by halogen, -OH, COOZ, -CN, NZ_2,

R is a bond, a divalent C1-C15-alkylene group, divalent C1-C15-alkylenoxy group, for example ethylenoxy group, or divalent C5-C20-aryl or heteroaryl group, with the above radicals themselves being able to be substituted by halogen, -OH, COOZ, -CN, NZ_2,

the radicals Z are each, independently of one another, hydrogen, a C1-C15-alkyl group, C1-C15-alkoxy group, ethylenoxy group or C5-C20-aryl or heteroaryl group, with the above radicals themselves being able to be substituted by halogen, -OH, -CN, and

x is 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10.

11. The membrane as claimed in claim 1, characterized in that monomers which are capable of effecting crosslinking and have at least 2 carbon-carbon double bonds are polymerized in step D).

12. The membrane as claimed in claim 1, characterized in that the polymerization in step D) is brought about by substance capable of forming free radicals.

13. The membrane as claimed in claim 1, characterized in that the polymerization in step D) is effected by irradiation with IR or NIR light, UV light, ß-rays, γ- rays and/or electron beams.

14. The membrane as claimed in claim 1, characterized in that the mixture produced in step A) and/or step B) comprises dissolved, dispersed and/or suspended polymer.

15. The membrane as claimed in claim 1, characterized in that a layer having a thickness of from 20 to 4000 µm, preferably from 30 to 3500 µm, in particular from 50 to 3000 µm, is produced in step C).

16. The membrane as claimed in claim 1, characterized in that the membrane formed in step D) has a thickness in the range from 15 to 3000 µm, preferably from 20 to 2000 µm, in particular from 20 to 1500 µm.

17. An electrode having a proton-conducting polymer coating based on polyazoles which is obtainable by a process comprising the steps

A) mixing of one or more aromatic tetraamino compounds with one or more aromatic carboxylic acids, esters thereof, acid halides thereof or anhydrides thereof which contain at least two acid groups per carboxylic acid monomer or mixing of one or more aromatic and/or heteroaromatic diamino carboxylic acids, esters thereof, acid halides thereof or anhydrides thereof with vinyl-containing phosphonic acid,

B) heating of the mixture obtainable according to step A) under inert gas at temperatures of up to 350°C to form polyazole polymers,

C) application of a layer using the mixture from step A) and/or B) to an electrode,

D) polymerization of the vinyl-containing phosphonic acid.

18. The electrode as claimed in claim 17, wherein the coating has a thickness in the range from 2 to 3000 µm, preferably from 3 to 2000 µm, in particular from 5 to 1500 µm.

19. A membrane-electrode unit comprising at least one electrode and at least one membrane as claimed in one or more of claims 1 to 16.

20. A membrane-electrode unit comprising at least one electrode as claimed in claim 17 or 18 and at least one membrane as claimed in one or more of claims 1 to 6.

21. A fuel cell comprising one or more membrane-electrode units as claimed in claim 19 or 20.

22. A process for producing proton-conducting polymer membranes comprising polymers containing phosphonic acid groups, which comprises the steps

A) mixing of one or more aromatic tetraamino compounds with one or more aromatic carboxylic acids, esters thereof, acid halides thereof or anhydrides

thereof which contain at least two acid groups per carboxylic acid monomer or mixing of one or more aromatic and/or heteroaromatic diamino carboxylic acids, esters thereof, acid halides thereof or anhydrides thereof with vinyl-containing phosphonic acid,

B) heating of the mixture obtainable according to step A) under inert gas at temperatures of up to 350°C to form polyazole polymers,

C) application of a layer using the mixture from step A) and/or B) to a support,

D) polymerization of the vinyl-containing phosphonic acid.